
Bidirectional Molecular Dynamics: Interpretation in Terms of a Modern Formulation of Classical Mechanics

TEERAKIAT KERDCHAROEN, KLAUS R. LIEDL,* and
BERND M. RODE

Institute for General, Inorganic, and Theoretical Chemistry, Innrain 52a, A-6020 Innsbruck, Austria

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ABSTRACT

The validity and applicability of bidirectional molecular dynamics is shown in terms of modern classical mechanics. A simple interpretation of bidirectional molecular dynamics is given. This interpretation justifies an easy approach to start from an equilibrium configuration, to perform simulations in parallel in "forward" and "backward" time direction, and to combine the two obtained trajectories into a single one for proper evaluation of statistical quantities. Practical results, obtained for liquid ammonia, are presented. © 1996 by John Wiley & Sons, Inc.

Introduction

In this article we focus on a unique possibility of "duplication" of simulation speed, based on the idea of backward parameterization of trajectories in classical dynamics. Since some discussion of this new approach on the Internet's Computational Chemistry List forum¹⁻⁵ has shown that this approach can easily be misunderstood and leads to misinterpretations in terms of real-time events, the mathematical background of the formalism will be briefly outlined in the following section, followed by a practical example of application.

* Author to whom all correspondence should be addressed.

Backward Parameterization of Dynamics

The powerful tools of vector analysis, differential geometry, and differential forms⁶⁻¹⁰ are very well known in physics since they are absolutely necessary for the formulation of general theory of relativity.^{7,11} It is rather astonishing that it took until the middle of our century before other parts of physics starting from electrodynamics were reformulated in these mathematical terms.¹² The fact that these mathematical tools not only allow reformulation of physical theories much more generally and esthetically, but also can help to deal with practical problems, will be shown in the following sections.

To illustrate this, an attempt to formulate the backward parameterization of dynamics in a classical formulation of mechanics¹³⁻¹⁵ is given.

ADVANCED APPROACH

In terms of modern formulation of classical mechanics^{16,17} the trajectory of a $3N$ -particle system is described as a line q in a $3N + 1$ -dimensional manifold of time and space. Independently of the parameterization (lets call the parameter s) of this line q we can calculate the velocities of the particles by

$$u := \frac{\dot{q}}{\langle Z, \dot{q} \rangle} \quad (1)$$

where

$$\dot{q} = \frac{\partial q}{\partial s} \quad (2)$$

In eq. (1), the brackets \langle, \rangle mean that the time 1-form Z should be applied to the vector-field \dot{q} . The accelerations are obtained by

$$a := \nabla_u u = \frac{\nabla_{\dot{q}} u}{\langle Z, \dot{q} \rangle} \quad (3)$$

where ∇ is the connection in the manifold. The dynamics are ruled by

$$ma = f \quad (4)$$

where f are the forces acting on the particles.

The basic idea of the concept presented here is to parameterize the trajectory q in two different ways, on the one hand in a forward direction of time, on the other hand in the backward direction of time. This does not suggest creation of two different trajectories. One simply uses two different descriptions for the same physical situation and both parameterizations actually describe a particle moving forward in time.

This can be simply seen by describing the $3N + 1$ -dimensional manifold by a time-adapted orthonormal inertial frame

$$Z = dx^0 = dt, \langle dx^a, dx^b \rangle = \delta_{ab} \quad (5)$$

The main assumption (to obtain the presented simple form of the algorithm but not concerning the general idea) is that one can describe the interactions within the system by a potential $V(x)$ that only depends on the instantaneous positions of particles (i.e., they form a conservative system).

The forces are calculated by

$$f(y) = - \left(\frac{\partial V(x)}{\partial x} \right)_{x=y} \quad (6)$$

Since the potential does not depend on time or on the velocities, the forces also do not depend explicitly on time or velocities.

Looking at the previously mentioned two parameterizations of the same trajectory

$$q(s) = \begin{pmatrix} s \\ q^s(s) \end{pmatrix} \quad (7)$$

$$\tilde{q}(s) = \begin{pmatrix} -s \\ \tilde{q}^s(s) \end{pmatrix} := \begin{pmatrix} -s \\ q^s(-s) \end{pmatrix} = q(-s) \quad (8)$$

[where s is the parameter and $q^s(s)$ in eq. (7) and $\tilde{q}^s(s)$ in eq. (8) are the $3N$ spatial components of the trajectory] it can be seen that these parameterizations obviously give the same trajectory, but parameterized in opposite directions.

The equations for velocities and accelerations result in

$$u = \frac{\dot{q}}{\langle dt, \dot{q} \rangle} = \begin{pmatrix} 1 \\ \dot{q}^s(s) \end{pmatrix} = \dot{q}(s) \quad (9)$$

and

$$a = \nabla_u u = \frac{\nabla_{\dot{q}} u}{\langle dt, \dot{q} \rangle} = \begin{pmatrix} 0 \\ \ddot{q}^s(s) \end{pmatrix} = \ddot{q}(s) \quad (10)$$

Analogously, for the backward parameterization one obtains

$$\tilde{u} = \frac{\dot{\tilde{q}}}{\langle dt, \dot{\tilde{q}} \rangle} = - \begin{pmatrix} -1 \\ \dot{\tilde{q}}^s(s) \end{pmatrix} = \begin{pmatrix} 1 \\ -\dot{\tilde{q}}^s(s) \end{pmatrix} = -\dot{\tilde{q}}(s) \quad (11)$$

and

$$\begin{aligned} \tilde{a} &= \nabla_{\tilde{u}} \tilde{u} = \frac{\nabla_{\dot{\tilde{q}}} \tilde{u}}{\langle dt, \dot{\tilde{q}} \rangle} = - \begin{pmatrix} 0 \\ \ddot{\tilde{q}}^s(s) \end{pmatrix} \\ &= \begin{pmatrix} 0 \\ \ddot{\tilde{q}}^s(s) \end{pmatrix} = \ddot{\tilde{q}}(s) \end{aligned} \quad (12)$$

Hence, the equation for the velocities changes sign depending on the parameterization on changing from the forward to the backward direction, whereas the equation for accelerations, i.e., the equation of motion [eq. (4)] remains the same.

Comparing the results for the two parameterizations and looking at the arbitrary point $s = 0$ (the

origin on time can be chosen arbitrarily) to obtain the initial conditions one observes

$$q(0) = \tilde{q}(0) \quad (13)$$

and, as a consequence

$$f(q(0)) = f(\tilde{q}(0)) \quad (14)$$

(this holds because of the assumption that the forces only depend on the positions of the particles), and finally, because $u = \tilde{u}$ for $s = 0$ one finds that

$$\dot{\tilde{q}}^s(0) = -\dot{q}^s(0) \quad (15)$$

In other words, one can realize the backward parameterization of the trajectory simply by inverting the signs of the first derivatives of the forward parameterization's spatial components at an arbitrary starting point and by using the same algorithm to integrate the equation of motion [eq. (4)] as for the forward direction. The inversion of signs is physically irrelevant, however, since the physical velocities u and \tilde{u} , which are the same for any parameterization, have to be sampled instead of the first derivatives of the parameterization \dot{q} and $\dot{\tilde{q}}$.

CLASSICAL APPROACH

In the classical formulation of mechanics¹³⁻¹⁵ there is no *a priori* possibility to parameterize the time. The only chance to introduce a parameterization to time is to consider time as a bijective function of another variable (the parameter) and carefully apply the mathematical rules of substitution to it

$$t: I \rightarrow \mathbb{R}: s \mapsto t(s) \quad (16)$$

In these terms a trajectory of a $3N$ -particle system would be a function

$$q(t): \mathbb{R} \rightarrow \mathbb{R}^{3N}: t \mapsto q(t) \quad (17)$$

and, at the same time, a function

$$q(s): I \rightarrow \mathbb{R}^{3N}: s \mapsto q(s) := q(t(s)) \quad (18)$$

The velocity is defined as

$$u := \frac{\partial q}{\partial t} \quad (19)$$

and the acceleration as

$$a := \frac{\partial u}{\partial t} = \frac{\partial^2 q}{\partial t^2}. \quad (20)$$

The equation of motion equals

$$f = ma \quad (21)$$

The key ideas are now, on the one hand, to integrate the equation of motion not in the variable t but in the variable s and, on the other hand, to consider two different choices for the function $t(s)$.

To establish the equation of motion in the variable s we calculate

$$\frac{\partial q}{\partial s} = \frac{\partial q}{\partial t} \frac{\partial t}{\partial s} \quad (22)$$

and, hence

$$u = \frac{\partial q}{\partial t} = \frac{\frac{\partial q}{\partial s}}{\frac{\partial t}{\partial s}} = \frac{\partial q}{\partial s} \frac{\partial s}{\partial t} \quad (23)$$

To obtain the acceleration in terms of the variable s we derive eq. (22) again with respect to the variable s

$$\begin{aligned} \frac{\partial^2 q}{\partial s^2} &= \frac{\partial}{\partial s} \left(\frac{\partial q}{\partial t} \frac{\partial t}{\partial s} \right) = \frac{\partial t}{\partial s} \frac{\partial}{\partial s} \left(\frac{\partial q}{\partial t} \right) + \frac{\partial q}{\partial t} \frac{\partial^2 t}{\partial s^2} \\ &= \left(\frac{\partial t}{\partial s} \right)^2 \frac{\partial^2 q}{\partial t^2} + \frac{\partial q}{\partial t} \frac{\partial^2 t}{\partial s^2} \end{aligned} \quad (24)$$

and therefore get

$$\begin{aligned} a &= \frac{\partial^2 q}{\partial t^2} = \frac{\frac{\partial^2 q}{\partial s^2} - \frac{\partial q}{\partial t} \frac{\partial^2 t}{\partial s^2}}{\left(\frac{\partial t}{\partial s} \right)^2} \\ &= \left(\frac{\partial^2 q}{\partial s^2} - \frac{\partial q}{\partial t} \frac{\partial^2 t}{\partial s^2} \right) \left(\frac{\partial s}{\partial t} \right)^2 \end{aligned} \quad (25)$$

If the system under consideration is a conservative system it is obvious that

$$f(q(t)) = f(q(s)) \quad (26)$$

Therefore, the equation of motion in the variable s results in

$$f(q(s)) = m \left(\frac{\partial^2 q}{\partial s^2} - \frac{\partial q}{\partial t} \frac{\partial^2 t}{\partial s^2} \right) \left(\frac{\partial s}{\partial t} \right)^2 \quad (27)$$

Let us now consider two different choices for the function $t(s)$. The first choice should be:

$$t = t(s): \mathbb{R} \rightarrow \mathbb{R}: s \mapsto t(s) = s \quad (28)$$

For obvious reasons we call this choice the “forward parameterization,” because

$$\frac{\partial s}{\partial t} = \frac{1}{\frac{\partial t(s)}{\partial s}} = 1 \quad (29)$$

and

$$\frac{\partial^2 t}{\partial s^2} = \frac{\partial^2 t(s)}{\partial s^2} = 0 \quad (30)$$

we find, by introducing (29) into (23)

$$u = \frac{\partial q}{\partial t} = \frac{\partial q}{\partial s} \quad (31)$$

and (30) into (25)

$$a = \frac{\partial^2 q}{\partial t^2} = \frac{\partial^2 q}{\partial s^2} \quad (32)$$

and, therefore

$$f(q(s)) = m \frac{\partial^2 q}{\partial s^2} \quad (33)$$

The second choice for $t(s)$ we consider is

$$t: \mathbb{R} \rightarrow \mathbb{R}: s \mapsto t(s) = -s \quad (34)$$

we call this second choice the “backward parameterization,” for which we get

$$\frac{\partial s}{\partial t} = \frac{1}{\frac{\partial t(s)}{\partial s}} = -1 \quad (35)$$

and

$$\frac{\partial^2 t}{\partial s^2} = \frac{\partial^2 t(s)}{\partial s^2} = 0 \quad (36)$$

and, therefore, by substituting (35) into (23)

$$u = \frac{\partial q}{\partial t} = -\frac{\partial q}{\partial s} \quad (37)$$

and (36) into (25)

$$a = \frac{\partial^2 q}{\partial t^2} = \frac{\partial^2 q}{\partial s^2} \quad (38)$$

and, finally

$$f(q(s)) = m \frac{\partial^2 q}{\partial t^2} \quad (39)$$

In other words, if we want to integrate the “forward parameterization” we do not have to

change anything in comparison to the integration with respect of t . However, this is trivial because we just changed the name of the variable from t to s . On the other hand, if we want to integrate the “backward parameterization,” as can be seen in (39), the equation of motion stays the same—this implies that the integration algorithm has not been changed—only the signs of the first derivatives of the parameterization of the trajectories have to be changed according to (37) in comparison to the “forward parameterization” at an arbitrary starting point to impose the right initial conditions.

Finally, we hope to give an explicit recipe of how to implement the aforementioned two parameterizations:

- By equilibrating the system under consideration, as usual, one ends up with a set of positions $q(t=0)$, velocities $u(t=0)$, and accelerations $a(t=0)$.
- On the one hand, take this configuration as starting point for a conventional simulation (which corresponds to the forward parameterization). In this case the velocities and accelerations are equivalent to the first and second derivatives of the trajectory’s parameterization.
- On the other hand, change all signs of the velocities to get the first derivatives of the backward parameterization, but leave the positions and accelerations the same. Use the same algorithm to integrate the backward parameterization as for the forward parameterization. In this case, a positive parameter step corresponds to a negative time step. The important point is now that for all backward parameterization the velocities are not equivalent to the first derivatives of the trajectories backward parameterization. To sample the velocities, or any velocity-dependent quantity, the signs of the first derivatives of the backward parameterization have to be changed to get the physical velocities.
- After the two parameterizations are integrated for some interval of the parameter corresponding to some period of time the results of the two parameterizations can be combined to form a single longer trajectory.

Discussion

There are several points of special importance concerning the concept of backward parameteriza-

tion. First, it is obvious that the starting point for backward and forward parameterization has to be a well-equilibrated configuration as for any other simulation. The starting point for the backward and forward parameterization is in no way a special point in the combined trajectory. There is no discontinuity in this point, neither in the positions and velocities nor in the forces, because not the first derivative of the parameterization is sampled, but the velocity, u . A combination of the forward and backward parameterization is also suitable for the calculation of dynamical properties like velocity autocorrelation functions or diffusion coefficients.

Even though the starting point for forward and backward parameterization is in no way a special point of the trajectory one could think of choosing it as a special point. For example, if one would succeed in establishing the concept of an "equilibrated transition state" the study of a chemical reaction could start at such a point.

Due to the well-known chaotic behavior of nonlinear dynamics it is very unlikely that one would find exactly the same configuration by parameterizing for a certain amount of time in the forward direction and afterward for the same amount of time in the backward direction or vice versa. However, the quality of the backward-parameterized trajectory is in no way inferior to the quality of the forward-parameterized trajectory. Just as for the forward-parameterized trajectory¹⁸ the backward-parameterized trajectory is diverged from the "exact trajectory" already after a very short time.

We would like to emphasize the difference between the concepts of time reversibility and backward parameterization. Under certain circumstances—namely in conservative systems—a trajectory again gives a trajectory if one inverts the axis of time in the configuration space. This phenomenon is called time reversibility. However, this does not hold for a trajectory in phase space as it is considered in statistical thermodynamics. Taking an harmonic oscillator it is obvious that the oscillator will return on the same spatial trajectory as it came, but in the opposite direction, when we invert the axis of time and therefore invert the velocity. This is called time reversibility. In phase space, however, the harmonic oscillator moves on an ellipse. Inverting the sign of velocity—this is equivalent to inverting the sign of momentum—generally does not even result in the same point. Inverting the velocity mirrors the point on the spatial axis, and the resulting trajectory in phase space is not even connected to the original trajec-

tory. In contrast to the reversal of time the backward parameterization of the trajectory has no discontinuity in the momentum coordinate. It simply follows the trajectory in its backward direction on the ellipse. The time axis and physical velocities are not reverted.

Backward parameterization is even possible in systems in which the time reversibility does not hold (e.g., in systems with dissipative forces or magnetic fields). The only difference in the approach presented here is that, in these cases, the equation of motion formulated in the backward parameterization would not be the same as for the forward parameterization, because forces would depend on the velocities. Nevertheless, it would not be difficult to establish the corresponding equations.

Finally, it should be noted that the approach in the formalism of mathematics and theoretical physics as given in the "Advanced Approach" subsection may build a barrier initially, but already, the rather simple application presented in this study shows that the effort will pay off. As soon as the systems under consideration become less trivial—e.g., nonconservative systems, noninertial coordinates like rotating coordinates, or more complicated parameterizations of time—this modern formalism becomes much more convenient or even unavoidable.

Example and Application: Liquid Ammonia

Traditional molecular dynamics usually start from a random or a crystal-like configuration. Once the simulation process has brought the system into the equilibrium state it is continued along the trajectory which will be considered here as "forward" trajectory:

$$t_0 \rightarrow t_1$$

In bidirectional molecular dynamics simulation trajectories are propagated in this "forward" and the reverse "backward" direction of time:

$$t_{-1} \leftarrow t_0$$

$$t_0 \rightarrow t_1$$

Since both simulations are independent, they can be performed simultaneously in parallel, i.e., on two processors. When the simulations have produced sufficient data for sampling, the ensemble averages are calculated from the combination

of both trajectories, which is equivalent to a single trajectory of length $t_1 - t_{-1}$.

To illustrate this in practice, we have performed constant energy (NVE) molecular dynamics simulations of liquid ammonia at 235 K. The simulation box contained 215 flexible ammonia molecules at the experimental density of 0.688 g/cm³. The intramolecular and intermolecular potentials were taken from spectroscopic data¹⁹ and theoretical work,²⁰ respectively. A time-step of 0.1 femtoseconds and a verlet-like predictor-corrector algorithm²¹ were employed to integrate the equation of motion.

The simulation started from a random configuration and reached "equilibrium" state after 7000 time-steps, from where it was continued in the "forward" direction for 20,000 time-steps, collecting the configurations and velocities at every tenth step.

The "backward" simulation started from the same configuration ($q(0), \dot{q}(0)$) as the "forward" analog, but by reverting the signs of all "velocities" $\dot{q}(0)$ to get the initial conditions ($\tilde{q}(0), \tilde{\dot{q}}(0)$) for the backward direction [cf. eqs. (13) and (15)]. It was performed for 10,000 time-steps, collecting configurations and velocities in the same way but by inverting the signs of the first derivatives $\dot{q}(s)$ as discussed previously [cf. eq. (11)]. After the simulations were completed, 10,000 time-steps of the "forward" simulation and 10,000 time-steps of the "backward" simulation were combined to give a single 20,000-time-step trajectory.

The nitrogen-nitrogen and nitrogen-hydrogen radial distribution functions depicted in Figures 1 and 2 accurately reproduce those of Klein's work^{22,23} and, as can be seen from the figures, the radial distribution functions obtained from the full 20,000-step "forward" simulation and from the combined backward-forward simulation are almost equivalent. As an example of a time-dependent property the center-of-mass velocity autocorrelation functions were calculated from forward and combined backward-forward simulations. They also agree within the statistical error fluctuation as depicted in Figure 3.

It is important to note that, strictly seen, this approach is only valid for constant-energy (NVE) molecular dynamics. Any perturbation to the system through momentum scaling²⁴ or pressure constraints²⁵ forbids, in principle, the connection of backward and forward trajectory if implemented in this simple way with the same differential equation. However, these effects seem to be quite small, if not negligible.²⁶

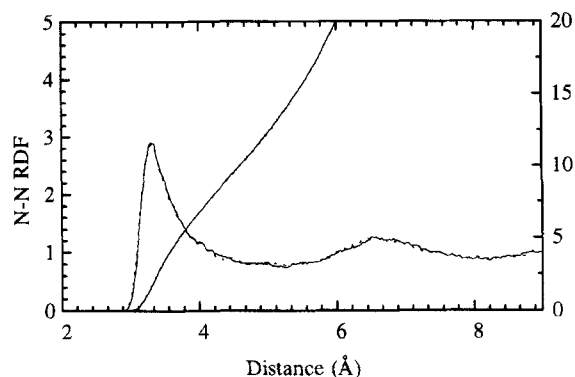


FIGURE 1. Nitrogen-nitrogen radial distribution function (N-N RDF) comparison between 20,000 time-steps forward simulation (solid line) and 20,000 time-steps combined backward-forward simulation (dashed line).

Conclusions

In the presented approach to bidirectional molecular dynamics we give a simple interpretation of "backward" simulations. Due to the usage of a more general, modern formulation of classical mechanics problems with "reversed momenta" or reversal of time are avoided.

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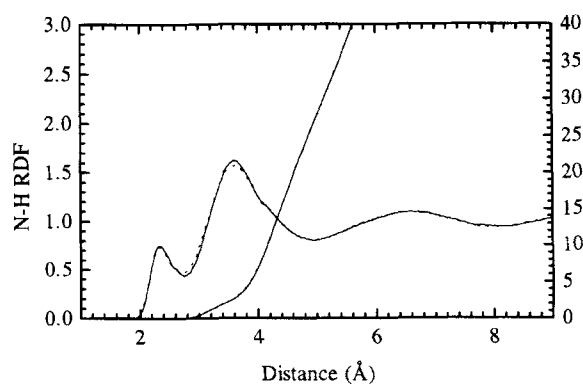


FIGURE 2. Nitrogen-hydrogen radial distribution function (N-H RDF) comparison between 20,000 time-steps forward simulation (solid line) and 20,000 time-steps combined backward-forward simulation (dashed line).

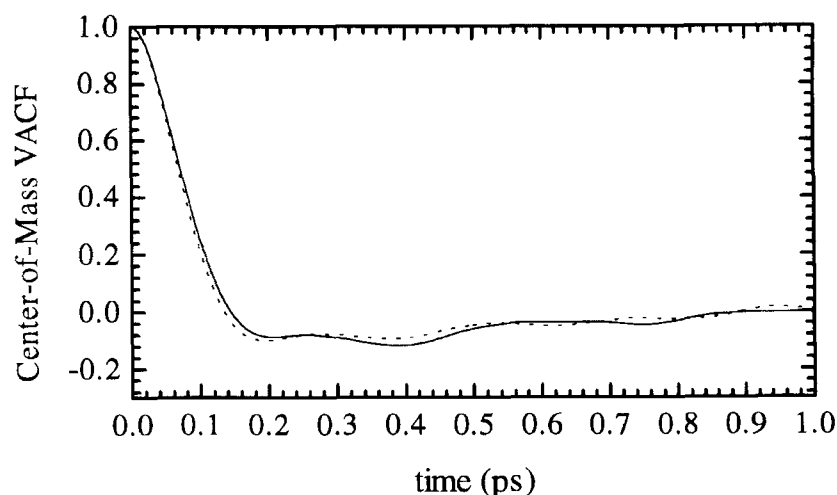


FIGURE 3. Center-of-mass velocity autocorrelation function (VACF) comparison between 20,000 time-steps forward simulation (solid line) and 20,000 time-steps combined backward-forward simulation (dashed line).

References

1. Song Ling, "Computational Chemistry List," October 27 and October 28, 1994 (private communication).
2. M. Winn, "Computational Chemistry List," October 28 and November 1, 1994 (private communication).
3. J. S. Shaffer, "Computational Chemistry List," October 31, 1994 (private communication).
4. R. Q. Topper, "Computational Chemistry List," October 31, 1994 (private communication).
5. S. Stuart, "Computational Chemistry List," November 1, 1994 (private communication).
6. K. Jänich, *Vektoranalysis*, Springer, Berlin, 1992.
7. M. Göckeler and T. Schücker, *Differential Geometry, Gauge Theories and Gravity*, Cambridge University Press, Cambridge, 1987.
8. S. Parrot, *Relativistic Electrodynamics and Differential Geometry*, Springer, Berlin, 1987.
9. H. Holmann and H. Rummeler, *Alternierende Differentialformen*, Bibliographisches Institut, Mannheim, 1981.
10. R. L. Bishop and S. I. Goldberg, *Tensor Analysis on Manifolds*, Macmillan, New York, 1968.
11. Ray d'Inverno, *Introducing Einstein's Relativity*, Oxford University Press, Oxford, 1992.
12. W. Thirring, *A Course in Mathematical Physics, Vol 2: Classical Field Theory, Second English Edition*, Springer, New York, 1986.
13. H. Goldstein, *Classical Mechanics*, Addison-Wesley, Reading, MA, 1959.
14. L. D. Landau and E. M. Lifschitz, *Mechanics*, Pergamon Press, Oxford, 1960.
15. A. Sommerfield, *Lectures on Theoretical Physics, Vol. I: Mechanics*, Academic Press, New York, 1964.
16. J. Rothleitner, *Die Prinzipien der Mechanik*, Institut für Theoretische Physik, Universität Innsbruck, 1994.
17. W. Thirring, *A Course in Mathematical Physics, Vol 1: Classical Dynamical Systems, Second English Edition*, Springer, New York, 1992.
18. M. P. Allen, D. J. Tildesley, *Computer Simulation of Liquids*, Oxford University Press, Oxford, 1987.
19. V. Spirko, *J. Mol. Spectrosc.*, **101**, 20 (1983).
20. S. V. Hannongbua, T. Ishida, E. Spohr, and K. Heinzinger, *Z. Naturforsch.*, **43a**, 572 (1988).
21. K. Heinzinger, W. O. Riede, L. Schaefer, and GY. I. Szász, *ACS Symposium Series No. 86 Computer Modeling of Matter*, P. Lykos, ed., American Chemical Society, Washington, DC, 1978.
22. A. Hinchliffe, D. G. Bounds, M. L. Klein, I. R. McDonald, and R. Righini, *J. Chem. Phys.*, **74**, 1211 (1981).
23. R. W. Impey and M. L. Klein, *Chem. Phys. Lett.*, **104**, 579 (1983).
24. H. J. C. Berendsen, J. P. M. Postma, W. F. Van Gunsteren, A. Di Nola, and J. R. Haak, *J. Chem. Phys.*, **81**, 3684 (1984).
25. H. C. Andersen, *J. Chem. Phys.*, **72**, 2384 (1980).
26. T. Kerdcharoen, K. R. Liedl, and B. M. Rode (unpublished data).